

91 arsenic (As), or antimony (Sb) have been added and P-type semiconductors in which acceptor elements such as boron (B), aluminum (AL), gallium (Ga), and indium (In) have been added.

Page 35, lines 9-38-page 36 lines 1-12, delete the current paragraph and insert
therefor:

92 The source gas flow rate which corresponds to the total surface area in the LPCVD reactor which can be covered with a semiconductor film must also be varied. In other words, the parameter which must be controlled is the higher silane flow rate per unit area, R. The exact same experiment described below was repeated with seventeen 235 mm x 235 mm substrates placed a distance of 20 mm apart in the LPCVD reactor. The substrate area was 23.5 cm x 23.5 cm x 2 = 1102.5 cm². This was combined with the reactor area of 25262 cm² to yield a total surface area of 44039 cm². R values of about 5.66 x 10⁻⁴ sccm/cm², 1.13 x 10⁻³ sccm/cm², 2.27 x 10⁻³ sccm/cm², and 4.53 x 10⁻³ sccm/cm² correspond to higher silane flow rates of 25 sccm, 50 scc, 100 sccm, and 199 sccm, respectively. When the deposition rate and film thickness uniformity among substrates was examined for the given disilane flow rates, behavior identical to that found previously was confirmed. That is, in addition to the deposition temperature and deposition pressure, the higher silane flow rate per unit area is a parameter necessary to unambiguously define the physical system. According to the discovery above, an R value of about 1.13 x 10⁻³ sccm/cm² or more is required for the deposition of silicon-containing film at a deposition temperature of about 430°C or less and a disilane partial pressure of about 100 mtorr or more. For example, for the deposition of a semiconductor film using one hundred 400 mm 500 mm substrates set 15 mm apart in a 900 mm diameter cylindrical deposition chamber, the substrate surface area is 400000 cm²; and the surface area inside the deposition chamber is about 56550 cm², leading to a total surface area A of about 456500 cm². Therefore, the minimum necessary silane flow rate is given by the R value of 1.13 x 10⁻³ sccm/cm² multiplied by the area A or 518 sccm. Similarly, a minimum

Q2 flow rate of about 1050 sccm is necessary for semiconductor film deposition in the case in which there are no hundred 560 mm x 720 mm substrates placed 25 mm apart in a 1200 mm diameter chamber since A is approximately 919500 cm^2 and $R \geq 1.13 \times 10^{-3} \text{ sccm/cm}^2$.

(2-5), Poly-Si TFT Channel Layer Thickness and Transistor Properties)

Page 51, lines 28-38-page 52, lines 1-37, delete the current paragraph and insert therefor:

With this invention, the gate insulator layer is formed using CVD or PVD after the semiconductor film crystallization is finished. No matter what process is used to form the gate insulator layer, it is desirable that the insulator layer formation temperature be at 350°C or lower. This is because it is important to prevent the thermal degradation of the MOS interface and the gate insulator layer. This same thing applies to all of the subsequent process steps. All of the process steps after forming the gate insulator layer have to be held to 350°C or less. In general, a gate insulator layer formed using CVD or PVD has many dangling bonds within the film; and the structure of the film is also unstable. This invention terminates the dangling bonds by exposure to oxygen plasma. In addition, CVD silicon oxide films contain Si-OH groups. Dangling bonds that have been terminated by such hydroxyl groups and oxygen plasmas are unstable in heat, easily dissociated in an environment of 350°C or higher. That is, dangling bonds such as Si-O^\star and Si^\star are generated again at the MOS interface and in the gate insulator layer. These become interface states or fixed charges in the insulator layer and cause a deterioration of the transistor properties. In the prior art, hydrogen plasma processing took place for an hour in order to overcome this. In this invention, however, because all of the process steps after the semiconductor film has been formed take place at 350°C or less, such thermal degradation does not occur. For this reason, hydrogenation is not required. With this invention, a higher performance, thin film semiconductor device can be produced easily and reliably. Although it is to be expected, the thermal degradation extends to the underlevel

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protection layer as well. As described in section (2-1), thermal degradation of the underlevel protection layer will lead to the deterioration of the properties of the thin film semiconductor devices. Although it is not as sensitive as the gate insulator layer, the influence is such that it cannot be ignored. For this reason, optimization of the thin film semiconductor device is achieved, theoretically, by having all processing steps, including the semiconductor film deposition steps, including the semiconductor film depositions steps, take place at a temperature of 350°C or lower. Doing so will avoid thermal degradation of both the underlevel protection layer and the gate insulator layer. Processes that can form semiconductor films at temperatures of 350°C or lower include PECVD and sputtering.

(2-11. The VHF-PECVD Reactor Used in this Invention)

Page 53, lines 1-38-age 55, lines 1-28, delete the current paragraph and insert therefor:

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First of all, Figure 2 will be used to describe the general configuration of the VHF-plasma enhanced chemical vapor deposition reactor (VHF-PECVD reactor) used in this invention. The PECVD reactor is a capacitively-coupled type, and the plasma is generated between parallel plate electrodes using a 144 MHz VHF power supply. The top drawing in Figure 2 is an overall perspective of the reaction chamber as viewed from above, a drawing of cross section A-A' is shown in the bottom of Figure 2. Reaction chamber 201 is isolated from the outside by reaction vessel 202, which is in a reduced pressure condition of from about 5 mtorr to 5 torr during film formation. Inside of reaction vessel 202, lower plate electrode 203 and upper plate electrode 204 are placed in mutually parallel positions. These two electrodes form the parallel plate electrodes. The space between these parallel plate electrodes is reaction chamber 201. This invention uses parallel plate electrodes with dimension of 410 mm x 510 mm. Since the distance between the electrodes is variable from 10 mm to 50 mm, the volume of reaction chamber 201 varies from 10 mm to 50 mm, the volume of reaction chamber 201 varies from 20911 cm³ to 10455 cm³, depending on the distance between the electrodes. The

distance between the parallel plate electrodes can be set freely between 10 mm to 50 mm, as stated above, by moving the position of lower electrode 203 up and down. Moreover, when set to a designated electrode distance, the deviation of the electrode distance over the 410 mm x 51 mm plate electrode surfaces is a mere 0.5 mm. As a result, the deviation in the electrical field strength that appears between the electrodes is 5.0% or less over the plate electrode surfaces; and an extremely uniform plasma is generated within reaction chamber 201.

Substrate 205 on which thin film deposition is to take place is placed on tope of lower plate electrode 203 and 2 mm of the substrate edge is held down by shadow 206. Shadow frame 206 has been omitted from the upper drawing of Figure 2 to make the overall drawing of the PECVD reactor easy to understand. Heater 207 is installed within lower plate electrode 203. The temperature of lower plate electrode 203 can be adjusted as desired from 25°C to 400°C. Except for the peripheral 5 mm, the temperature distribution within lower plate electrode 203 is within $\pm 1.0^{\circ}\text{C}$ relative to the set-point temperature. Essentially, even if the size of substrate 205 were 400 mm x 500 mm, the temperature deviation within the substrate could be maintained to within 2.0°C . For example, if a conventional glass substrate (such as Corning Japan's #7059, Nippon Electric Glass Co., Ltd.'s OA-2, or NH Techno Glass's NA35) were used as substrate 205, shadow frame 206 would hold substrate 205 down to prevent if from deforming concavely by the heat from heater 207 as well as to prevent unnecessary thin films formed on the edges and back surface of the substrate. The reaction gas, which is made up of source gases and additional gases as required, flows through tube 208 and is introduced into upper plate electrode 204. It then flows between gas diffusion plates 209 located inside upper plate electrode 204, and flows from the entire surface of the upper plate electrode into reaction chamber 201 at a virtually uniform pressure. If film formation is taking place, some of the reaction gas will be ionized when it exits the upper plate electrode and cause a plasma to be generated between the parallel plate electrodes. From a part to all of the reaction gas will

participate in film formation. Residual reaction gas that has not participated in film formation and gases formed as a result of the film forming chemical reaction will become discharge gases and be discharged through exhaust port 210 which is in the top of the peripheral section of reaction vessel 202. The conductance of discharge port 210 is sufficiently large compared to the conductance between the parallel plate electrodes. The desired value is one that is 100 times or more of the conductance between the parallel plate electrodes. In addition, the conductance between the parallel plate electrodes is even sufficiently larger than the conductance of gas diffusion plate 209, and that desired value is also 100 times or more of the conductance of gas diffusion plate 209. Through such a configuration, reaction gas can flow into the reaction chamber virtually uniformly from the entire surface of the large 410 mm x 510 mm upper plate electrode; and, at the same time, discharge gas will be discharged in all directions from the reaction chamber in an even flow. The flow rates of the various reaction gases to tube 208 will be adjusted to their designated values by mass flow controllers. In addition, the pressure within reaction vessel 202 will be adjusted to the desired value by conductance valve 211, which is located at the exit of discharge port. A pumping system, such as a turbomolecular pump, is located on the exhaust side of conductance valve 211. In this invention, an oil-free magnetic levitation type turbomolecular pump is used as part of the pumping system, and the background vacuum within reaction vessels such as the reaction chamber is set to 10^{-7} torr level. In Figure 2, arrows are used to show the general flow of the gas. Both reaction vessel 202 and lower plate electrode 203 are at ground potential. These and upper plate electrode 204 are electrically isolated by insulation link 212. When a plasma is generated, for example, 144 MHz vhwaves that are generated from VHFwave oscillation source 213 are amplified by amplifier 214, pass through matching circuit 215, and are applied to upper plate electrode 204.

Page 55, lines 29-38-page 56, lines 1-24, delete the current paragraph and insert

therefor:

As stated above, because the PECVD reactor used in this invention had very sophisticated intra-electrode interval control and uniform gas flow, it is a thin film formation reactor that is able to handle large substrates of 400 mm x 500 mm in size. However, by merely adhering to these basic concepts, it can easily handle further enlargements in the substrate. Actually, it is possible to produce a reactor that can handle even larger substrates of 550 mm x 650 mm. In addition, in this invention, a common 144 MHz VHFwave frequency was used. Of course, VHS waves using other frequencies may also be used. For example, VHF waves from 100 MHz to 1 GHz may all be used. On the other hand, if the rf frequency is from 10 MHz to several hundred MHz (VHF), it is possible to generate a plasma between the parallel plate electrodes. Therefore, frequencies such as 27.12 MHz, 40.68 MHz, 54.24 MHz and 67.8 MHz, which are whole number multiples of the industrial rf frequency (13.56 MHz) may be used. In other words, by changing VHFwave oscillator 213, amplifier 214, and matching circuit 215 of the PECVD reactor used in this invention, a plasma using electromagnetic waves of a desired frequency can be easily generated. In general, in the case of an electromagnetic wave plasma, if the frequency is increased, the electron temperature within the plasma will increase and radicals can be easily created. For this reason, as will be explained later, even if the temperature of the substrate is as low as approximately 340°C, the deposited film will already be in a polycrystalline silicon condition immediately after deposition. Thus, poly-Si TFTs can be easily fabricated even without special crystallization process steps.

(2-12, Semiconductor Film Formation and the Gases Used for Formation When Using VHF-PECVD and Microwave PECVD)

Page 56, lines 25-38-page 59, lines 1-4, delete the current paragraph and insert

therefor:

One of the characteristics of this invention is that the film deposited by VHF-PECVD or microwave PECVD is polycrystalline immediately after deposition (an as-deposited film). It is extremely difficult to make a polycrystalline as-deposited film using normal PECVD processing. Since the substrate temperature is less than 400°C, the mobility of source materials such as silane on the surface of the growing film decreases; and the selectivity of the source material for the polycrystalline source material for the polycrystalline state as opposed to the amorphous state is lost. This invention eliminates this deficiency in the PECVD method by diluting source materials using noble gas elements and by using a VHF plasma or microwave plasma, both of which are capable of raising the electron temperature. To form a polycrystalline film in the as-deposited state, radicals and ions of the noble gas elements, such as helium (He), neon (Ne), and argon (Ar), are generated, without generating radicals and ions of source materials, and must carry energy to the surface of the substrate. Because radicals and ions of source materials cause vapor phase reactions or react the instant they arrive at the substrate surface, selectivity is lost, thereby preventing polycrystalline growth. For these reasons, the generation of such radicals and ions within a plasma must be avoided at all costs. The source materials are carried to the surface of the growing film in an inactive state and become adsorbed there. Subsequently, if energy for reaction is supplied, such as by dilute gas, a polycrystalline film will be formed in the as-deposited state. Consequently, dilution of the source gas is desired, and this gives rise to the necessity of selecting as the dilution gas a gas that promotes reaction of the source materials on the substrate surface. It goes without saying that the noble gas elements are composed of individual atoms, and, for this reason the ionization potential spectrum is very simple. For example, the monvalent ionization potential of helium is 24.587 eV, while the divalent ionization potential is only 54.416 eV. Further, the

monovalent ionization potential of neon is 21.561 eV, while the divalent ionization potential is 40.962 eV. The monovalent ionization potential of argon is 15.759 eV, while the divalent ionization potential is 27.629 eV, and the trivalent ionization potential is 40.74 eV. Therefore, when a small amount of source materials is diluted in helium and a plasma is generated, most of the ionized helium will be 24.587 eV monovalent ions. When a small amount of source materials are diluted in neon and a plasma is generated, the neon will be ionized into mainly monovalent ions of 21,564 eV. For argon, although both monovalent ions and divalent ions are dominant, argon radicals and ions are effectively generated even when the source material is not diluted by a large amount of argon because the ionization energy is relatively low. In contrast to this, there is hydrogen, widely used as a dilution gas in the prior art, in which more than ten different ionization potentials exist between 15 eV and 18 eV for the ionization potential of the hydrogen molecules. For this reason, in contrast to noble gas elements such as helium which form plasmas containing one or two energies (laser light if referred to in terms of light), molecular gases such as hydrogen form plasmas containing a mixture of energies (white light if refereed to in terms of light). Just as laser light will transport energy more effectively than white light, energy is transported to the substrate surface more effectively when the source gas is diluted by a noble gas element. In addition to the noble gas elements of helium, neon and argon, krypton (Kr) and xenon (Xe) may of course also be used as dilution materials during the deposition of semiconductor films. On the other hand, since VHS and microwave plasmas have high average electron temperatures within the plasma, the radical generation efficiency can be increased a relatively low power. In other words, since high power is not necessary, these plasmas generate few high energy ions, and resulting film damage is kept to a minimum. Further, a high radical generation efficiency also increases the film growth rate. If this invention were also carried out using the 13.56 MHz rf plasma used widely in the prior art, the film formation rate would be extremely slow, less than several

Q6 $\text{\AA}/\text{min}$, making it absolutely unsuitable for utilization. Moreover, a very slow film formation rate will be harmful, reducing the quality of the film. Which is to say that it is precisely because VHF plasmas and microwave plasmas are used that this invention can be attained. In this sense, this invention can be very easily achieved by also using microwave PECVD, having a frequency an integer multiple of 2.45 GHz. And with such systems, there is an even greater degree of freedom in film formation conditions than in VHF-PECVD, meaning a semiconductor film with even better crystallinity can be deposited with greater ease.

(2-13, Optimum Film Thickness for VHF-PECVD and Microwave PECVD As-Deposited Films)

Page 59, lines 7-38-page 6, lines 1-16, delete the current paragraph and insert therefor:

Q7 When placing a film in the polycrystalline state immediately after deposition (as-deposited) using VHF-PECVD or microwave PECVD, the film quality for film thicknesses ranging from 0 to 500 \AA will be extremely poor compared to normal crystallized films. The film will consist of small, island-shaped crystalline grains in a sea of amorphous material, have a very low degree of crystallinity, and contain a large number of defects. From 500 \AA to 1000 \AA , the ration of crystal grains to the amorphous material will increase. From about 1000 \AA to 1500 \AA , the semiconductor surface will be generally covered with crystal grains; and the amorphous components on the surface will almost disappear. From about 1500 \AA to 2000 \AA , the size of the crystal grains will gradually increase along with the film thickness. At 2000 or higher, the film will grow while the crystal grains maintain approximately the same shape. The film thickness dependency of the transistor properties will also change in response to changes in the film quality relative to the film thickness. At 2000 \AA or higher, because the film quality will exhibit virtually no change (because there is almost no thin film degradation),

the better the transistor properties become. At film thicknesses of 2000 \AA to 1500 \AA , thin film degradation will begin to take effect. Yet, as before, the thin film effect will remain dominant. Although this will be more lax than at 2000 \AA or higher, even here, the thinner the film the better the transistor properties become. Between 1500 \AA and 200 \AA , thin film degradation and the thin film effect become competitive and transistor properties in the on condition reach their maximum values. With a film thickness of less than 200 \AA , thin film degradation overcomes the thin film effect, and the thinner the film, the poorer the transistor properties. Put another way, in the case of this invention, transistor properties are the best at semiconductor film thicknesses from 20 \AA to 1500 \AA , but ideally between 400 \AA to 1300 \AA . Until this point, the discussion has been about transistor properties in the on state; but the leak current will also vary with the thickness of the film. The principles of off state leakage in thin film semiconductor device are not well understood. In this invention, the principles are unclear; but, if the film thickness is 1000 \AA or more, there is a strong positive correlation between the film thickness and off state leakage. The thicker the film, the larger the off state leakage. If the film thickness is less than 1000 \AA , the correlation weakens and becomes independent of the off state leakage. In other words, between 0 and 1000 \AA , the off state leakage current is almost consistently at the minimum. Consequently, the one state transistor properties are best, and the film thicknesses in which the off state leakage is the smallest are from 200 \AA to 1000 \AA , but ideally from 400 \AA to 1000 \AA . When the thin film semiconductor device of this invention is used in an LCD, it is desirable to consider the effects of light exposure on the off state leakage current. Light exposure will cause an increase in the off state leakage current in thin film semiconductor devices. This is called the optical leakage

current. Having a sufficiently small optical leakage current is a condition for a good thin film semiconductor device. In the case of the thin film semiconductor device of this invention, the optical leakage current is proportional to the film thickness. From the perspective of reliable production and optical leakage current coexisting, it is desirable to have a film thickness from about 100 Å to 800 Å. In a case in which the off state leakage and optical leakage are important, such as when using a thin film semiconductor device for the pixel switching element of an LCD, it is desirable to have a semiconductor film thickness from 100 Å to 700 Å. Moreover, when it is necessary to give even stronger consideration to on current, the optimum thickness is from 200 Å to 800 Å. A system that would satisfy all conditions would have the thickness from 400 Å to 800 Å, but ideally from 600 Å to 800 Å. Further, it is normally quite difficult to activate implanted ions in the source and drain regions at a low temperature of 350°C or lower as happens with this invention. This is the reason that to carry out activation in a stable manner, a lower limit must be set for the semiconductor film thickness. With this invention, the desired value is 300 Å or higher. If an LDD structure is to be utilized, a thickness of 500 Å or higher is desired.

(2-14, Crystallization of the Semiconductor Film through VHF-PECVD and Microwave PECVD)

Page 61, lines 17-38-page 62, lines 1-15, delete the current paragraph and insert therefor:

As described in detail in section (2-12), although a polycrystalline film in the as-deposited state can be obtained easily using VHF-PECVD, the film quality is not as good as a crystallization film. On the other hand, it is difficult to crystallize a film obtained from the normal PECVD process as long as it has not been dehydrogenated or carefully annealed. In

contrast, a semiconductor film from VHF-PECVD or microwave PECVD can be very easily crystallized using RTA or VST-SPC, or be melt crystallized such as by laser irradiation. Since most of the film will already be in an as-deposited crystalline state and residual amorphous components will be limited, crystallization of residual amorphous components can be achieved by means of a relatively low energy supply. Also, even when melt crystallization progresses using high energy, the polycrystalline components play the role of preventing the evaporation and scattering of semiconductor atoms. Thus, crystallization can proceed smoothly without semiconductor film damage, surface roughness, material loss and other problems. Ultimately, it can be said that rather than having a film obtained through the VHF-PECVD process or the microwave PECVD process as the active area of thin film semiconductor device in the as-deposited state, it is more suitable to have such a film be the first semiconductor layer when producing low temperature poly-Si TFTs in which the highest temperature of the process step is 350°C or lower using melt crystallization. Put differently, a high-performance thin film semiconductor device can be produced by forming a semiconductor film on top of an insulating substance using the VHF-PECVD process or the microwave PECVD process and then crystallizing this film using solid phase crystallization, such as RTA or VST-SPC, or crystallizing it using melt crystallization, such as by laser irradiation, and then having the subsequent process steps take place at 350°C or lower.

Page 62, lines 16-34, delete the current paragraph and insert therefor:

Films deposited by VHF-PECVD or by microwave PECVD have quality closer to that of films deposited using LPCVD than to films deposited by PECVD. For this reason, the relationship between the transistor properties and semiconductor film thickness obtained when producing a thin film semiconductor device through crystallization becomes equivalent to the relationship possessed by a thin film semiconductor device produced by the LPCVD process. In contrast to semiconductor films produced by the LPCVD process, however, which show

almost no reduction in film thickness before or after crystallization, some slight reduction can be found in VHF-PECVD and microwave PECVD films. Therefore, when crystallizing such films to produce thin film semiconductor devices, the discussion in section (2-6) can be applied as is by considering the semiconductor film thickness after crystallization to be the same as the film thickness of a film from the LPCVD--crystallization method.

Page 79, lines 23-38-page 80, lines 1-15, delete the current paragraph and insert therefor:

Then, an approximately 750 \AA intrinsic silicon layer, which becomes the active layer of the thin film semiconductor device, was deposited. The intrinsic silicon layer was deposited by means of a VHF-PECVD reactor, described previously in section (2-11), using a 50 sccm flow rate of monosilane (SiH_4) as the source gas and a 4800 sccm flow rate of argon (Ar), one of the noble gas elements, as a dilution gas. During deposition of the intrinsic silicon layer, the VHF wave power was 715 W, the pressure in the reactor chamber was 0.8 torr, the distance between parallel plate electrodes was 35.0 mm, the lower plate electrode temperature was 400°C , and the substrate surface temperature was 34°C . The semiconductor layer obtained in this way is a silicon layer of high purity and is polycrystalline in the state immediately after deposition ("as-deposited"). The degree of crystallinity was measured using multiple wavelength spectroscopic ellipsometry and was found to be 78%. Usually, if the degree of crystallinity found by means of spectroscopic ellipsometry is less than 30%, the silicon layer is considered to be amorphous; if it is 70% or more, the layer is considered to be polycrystalline; and if it is between 30% and 70%, it is considered to be mixed. Hence, the film that was obtained was clearly polycrystalline in the as-deposited state. In fact, a sharp Raman shift was detected by means of Raman spectroscopy in the wave number region in the vicinity of 520 cm^{-1} , which indicates a crystalline state; in addition, it was observed by means

910 of X-ray diffraction that the crystals have a relatively strong preferred orientation in the {220} direction.

Page 81, lines 20-38-page 82, lines 1-22, delete the current paragraph and insert therefor:

911 The maximum process temperature reached in Example 5 was the 400°C lower plate electrode during deposition of the semiconductor layer by means of VHF-PECVD reactor; the substrate surface temperature at that time was 340°C. As shown by this example, poly-Si TFTs, which are a kind of crystalline thin film semiconductor device, were successfully fabricated at extremely low process temperature using a simple manufacturing method that does not require crystallization by laser irradiation or other means. While values for on current and mobility are far from those in Example 1, in which laser irradiation was employed, they are from 4 to nearly 10 times higher than the values for a-Si TFTs fabricated by conventional methods with a maximum processing temperature of 400°C. Additionally, source and drain regions in Example 5 were formed by means of ion implantation with the gate electrode used as a mask. Moreover, because implanted ions were activated at low temperatures of from 300°C to 350°C, implanted ions from the source and drain regions essentially do not diffuse at all into the channel region. Therefore, the overlapping of gate electrodes and source and drain regions is determined by horizontal projection deviation during ion implantation, and the deviation value is not more than several hundred Å. In other words, the edges of the gate electrode and the edges of the source and drain matched extremely closely in a so-called self-aligned structure. For that reason, the parasitic capacitance between source and gate and between drain and gate is extremely small in comparison with that of a-Si TFTs. Due to these two facts, when the thin film semiconductor devices of this invention are used a pixel switching element for an active-matrix liquid crystal display device (LCD), high definition LCDs (LCDs having a large number of picture